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RESEARCH

Evaluation of sunflower oil as a multifunctional lubricating oil additive

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Abstract The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. Viscosity index improvers, antifoaming agents, emulsifiers, demulsifiers, and pour point depressants are examples of different kinds of additives. Most of the present day additives are synthetic acrylate based. But with increasing environmental awareness, the research in the area towards the synthesis of multifunctional biodegradable lubricating oil additive is increasing day by day. Hence, in our present work chemistry of biodegradable multifunctional lubricating oil additive based on vegetable oil (sunflower oil) has been investigated. In the present work solvent-free synthesis of homopolymer of sunflower oil was performed by two different ways; microwave irradiation method and thermal method using benzoyl peroxide as initiator. Characterization of the polymers was done by spectral (NMR, IR), GPC and viscometric analysis and finally performance evaluation was tested by standard ASTM methods. Performance evaluation as pour point depressant, viscosity modifier or viscosity index improver and antiwear in different base oils (BO1, BO2) was carried out by standard ASTM methods. Shear stability and oil thickening property of the polymers have also been investigated and reported here. Thermal stability of the polymers was determined by thermogravimetric analysis. A comparison of their performances has also been reported. The additive prepared by microwave-assisted method showed better viscosity index and pour point values as compared to thermally prepared additive. Thus, polymerized sunflower oil may be used as a potential biodegradable lube oil additive and hence the microwave-assisted protocol may be considered as a cost-effective greener approach for synthesis of lube oil additive.

Keywords Thermal stability · Intrinsic viscosity · Viscosity index improver · Antiwear property · ASTM method · Shears stability index · Biodegradability test · Pour point depressant

Abbreviations

ASTM	American society for testing and materials
THF	Tetrahydrofuran
HPLC	High-performance liquid chromatography
M_n	Number average molecular weight
M_w	Weight average molecular weight
C	Concentration (g cm^{-3})
KV	Kinematic viscosity (centistokes or cSt)
TMS	Tetramethylsilane

Background

Lubricant is a substance (often a liquid) reduces the friction and wear when introduced between two moving surfaces. A lubricant provides a protective film which allows for two touching surfaces to be separated and thus lessening the friction between them. Hence, in internal combustion engines lubricant is very essential for longer life of the engine. Lubricants are generally composed of a majority of

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base oil plus a variety of additives to impart desirable characteristics. The types of the lubricant depend upon the types of base oils. The base oils may be mineral (petroleum originated), synthetic (polyalphaolefins, polyalkylene glycols, synthetic esters, silicones etc.) or vegetable (sunflower oil, soybean oil, palm oil etc.). When the base oil is a vegetable oil, then the lubricant is known as biolubricant, in case of synthetic oil it is called synthetic lubricant and when the base oil is mineral or petroleum based then the lubricant is known as mineral lubricant. Most of the lubricants used today are mineral or petroleum based and are a mixture of paraffinic, naphthenic and aromatic hydrocarbons. Nowadays, with increasing environmental pollution although it is essential to use vegetable oils as base fluid rather than mineral oil or synthetic ester based oils, but due to the poor oxidative and hydrolytic stability, high temperature sensitivity of tribological behavior, poor cold flow properties and high cost vegetable oils are very limitedly used as base oils for industrial lubricants [1, 2]. So, the petroleum-based fluids are still now dominated in the lubricant market due to its ease availability and lower cost.

The base oils cannot satisfy all the requirements of modern engines. Hence, a large number of functional additives are added to the lube oil to enhance the characteristic properties already present or to impart some new additional properties. Their amount varies from >1 % to 30 % or more [3]. The lube oil additives commonly used are viscosity modifier (VM) or viscosity index improver [4], pour point depressant (PPD) [5], antioxidant [6, 7], antiwear [8, 9], extreme pressure agent etc. Since multifunctional additives induce more than one of the above performances, research throughout the world is increasingly directed toward producing such type additives. The commercial synthetic acrylate-based additives are nonbiodegradable and their widespread use has raised many environmental concerns. Due to increasing environmental pollution the direction towards the development of environmentally benign green polymeric additive in the lubricant chemistry is increasing day by day. There are lots of examples where biodegradable vegetable oils [10–12] are used for the synthesis of such type of polymeric additives. Sulfurized vegetable oil derivatives are used as lubricating oil additive since long time [13]. The US Patent 4970010 (1990) and 5282989 (1994) disclosed the use of sulfurized vegetable oils as lube oil additive (as extreme pressure and antiwear). Sulfurized vegetable wax esters as an antiwear, friction modifier and extreme pressure additive were described in US pat. No. 4152278. The biodegradable vegetable oil composition for lubricant was disclosed in US Patent 6534454 B1 in the year 2003. The application of meadowfoam oil and meadowfoam oil derivatives as lubricant additive was claimed in US Patent 4925581 (1990). US Patent 3849323 refers to blended petroleum products for lubrication containing natural oil, such as jojoba oil. Recently, in the International Conference on Chemical Processes and Environmental issues (ICCEEI'2012) the synthesis of pour point depressant from sunflower oil has been discussed.

Table 1 Fatty acid profile of SFO

Fatty acid	% Composition (max)
Saturated	
C12:0 (lauric acid)	–
C14:0 (myristic acid)	–
C16:0 (palmitic acid)	6.8
C18:0 (stearic acid)	5
C20:0 (arachidic acid)	1
Unsaturated	
16:1 (palmitoleic acid)	–
18:1 (oleic acid)	31.1
18:2 (linoleic acid)	56
18:3 (linolenic acid)	0.2

Due to excellent tribological properties and predominantly polyunsaturated fatty acid composition (Table 1), sunflower oil was chosen for our present work. In this work, homopolymer of sunflower oil was synthesized without adding any solvent by thermal as well as a greener way, microwave-assisted method. Their characterization and finally additive performances for their end application were observed by standard ASTM methods.

Methods

The radical polymerization of sunflower oil was carried out using benzoyl peroxide (BZP) as initiator in two different ways, thermal and microwave irradiation method. Then characterization of the prepared additives was done by spectral (FT–IR and NMR) technique. The average molecular weight of the prepared polymeric additives was determined by gel permeation chromatography (GPC) and viscometric analysis. In GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were measured. THF of HPLC grade was used as mobile phase in the Water GPC system (polystyrene calibration) at 40 °C. In viscometric method, the viscosity average molecular weight (M) was calculated using Mark Houwink–Sukurda relation (MHS) (Eq. 1) by Ubbelohde OB viscometer at 40 °C taking eight different concentrations (g cm^{-3}) of the polymeric additives in toluene [14, 15]. Chronometer was used for recording flow times. The intrinsic viscosity of the additives which is required for their average molecular weight calculation by MHS

equation was evaluated by graphic extrapolation method [16, 17, 18] using the Eqs. 2 and 3

$$\text{MHS} \quad [\eta] = KM^{a} \tag{1}$$

$$\text{Huggins (H)} \quad {}^{\eta_{sp}}/_{C} = [\eta]_{h} + k[\eta]_{h}^{2}C \tag{2}$$

$$\text{Kraemer (K)} \quad \text{In}\ \eta_{r}/C = [\eta]_{k} - k_{k}[\eta]_{k}^{2}C \tag{3}$$

where, $[\eta]$ is the intrinsic viscosity in dL g^{-1}, M is the viscosity average molecular weight, K and a are viscometric constants for given solute–solvent system and temperature, η_r is relative viscosity or ratio of viscosity of the polymeric solution and pure solvent, η_{sp} is the specific viscosity, k is reaction coefficient and C is concentration of the additives in toluene. The subscripts h and k are denoted for Huggins and Kraemer equation, respectively. In MHS equation, the constants $K = 0.00387$ dL g^{-1} and $a = 0.725$ were employed and adequate precautions against evaporation of the solvent during viscometric measurements were taken. The relationship $k_h + k_k = 0.5$ [18] has taken into account to predict the extent of interaction among the polymer and base oil.

Thermal stability of the additives was also determined. Solubility in different base oils was tested. Shear stability and oil thickening properties were also measured. The multifunctional performance (viscosity index improver, pour point depressant and antiwear) of the additive-doped base oil was evaluated by standard ASTM methods. A comparison of the performance of the additives prepared by the two processes was discussed in conclusion. Finally, the microbial degradation of the polymers was tested (1) by disc diffusion method [19] against fungal pathogens and (2) by soil burial degradation test as per ISO 846:1997 [20]. The degradation was confirmed by measuring the shift of IR frequency of the ester carbonyl after the biodegradability test.

Results and discussion

Spectral analysis

The IR absorption in the region 1,736.8–1,732 cm^{-1} of the homopolymers of sunflower oil (SFO) prepared by the two processes showed the presence of ester carbonyl groups. Peaks from 2,944.1 to 2,851.6 cm^{-1} for C–H stretching and 1,454.2–1,372 cm^{-1} are due to bending vibrations of $-CH_3$ and $-CH_2$ groups. Peaks from 1,245.9 to 1,069.5 cm^{-1} were due to the ester C–O stretching vibration. The presence of peaks at 1,654.8–1,675 cm^{-1} for olefinic bonds was observed for SFO and their absence indicates the formation of homopolymer. ^{1}H NMR of polymers of SFO (Figs. 1, 2) showed broad peaks in the range at 4.12–4.32 ppm due to ester methylene protons. The proton decoupled ^{13}C NMR of SFO showed peak at 172.9–178.7 for protons of $-OCH_2$ groups of the triester. The absence of unsaturation was indicated by the absence of peaks in the range 130–150 ppm.

The thermal stability obtained from TGA results of the two polymers is shown in Fig. 3, where the percent weight loss (PWL) of the polymers is plotted against increase in temperature (°C). The figure shows that at any particular temperature the percentage of decomposition of the homopolymer of SFO prepared by microwave irradiation (P-2) is lower as compared to the homopolymer prepared by thermal method (P-1). The PWL of the two polymers with increase in temperature is listed in Table 2. From the values it was seen that percentage of weight loss for P-1 at 290 and 400 °C are 35 and 92 %, respectively, and for P-2 at the same temperatures 17 and 74 %, respectively. Therefore, it is clear that thermal stability of P-2 is higher as compared to P-1. This may be due to relatively more linear arrangement of P-2 polymer as compared to P-1. On the other hand, in thermal method the larger reaction time for polymerization increases the possibility of branching (which give rise to more number of tertiary carbons) and that is the probable reason for lower thermal stability of P-1 as compared to P-2.

The intrinsic viscosity values for both the polymers, obtained from two different Eqs. (1, 2), have little difference. The higher values indicate that both the polymers have fairly strong interaction with the solvent. k_h values also indicate good solvation which is further supported by the $k_h + k_k$ values, and thus point towards the formation of the chain-like structure of the present polymer as discussed earlier [18]. Molecular weights (viscosity average, M_n and M_w) for P-1 and P-2 obtained by Mark–Houwink equation and GPC obtained showed excellent correlation (Table 3). The polydispersity index (PDI) data of both the polymers prepared by the two methods are very close to one which indicates that molecular weight distribution of the polymers is uniform and the molecules are linear with little branching. This is very significant observation because, with increasing linearity the extent of interaction of the additive with the base oil increases and as result of that yielded a better additive performances.

Thickening power of both the homopolymers as evaluated in different base stocks (Table 4) indicated a gradual increase with increase in concentration of the additives (Table 5). The result showed that the thickening power of the additives in BO1 base oil is far better than BO2 base oil. The difference in thickening effect of the two base oils doped with additives is due to the difference in interaction of the additives with the base oils. The interaction of the additive with BO1 base oils is far better as compared to BO2 and as a result of which increase in viscosity of BO1 base oil doped with the additives by unit amount is relatively higher. The results also showed that P-2 polymer is a

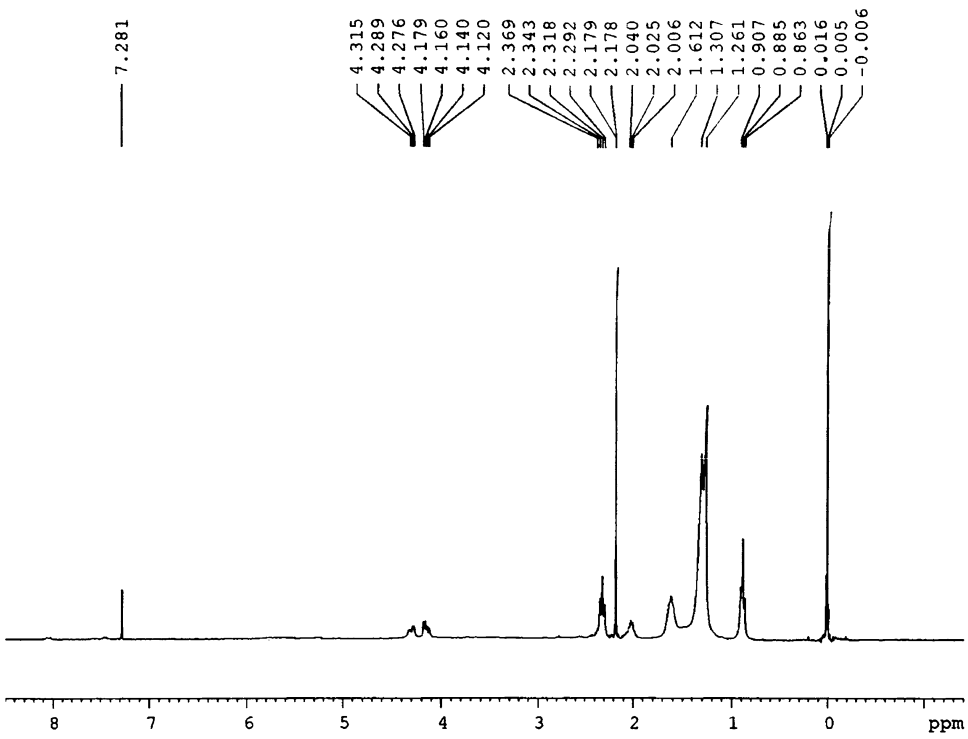

Fig. 1 ^{1}H NMR of thermally prepared SFO polymer (P-1)

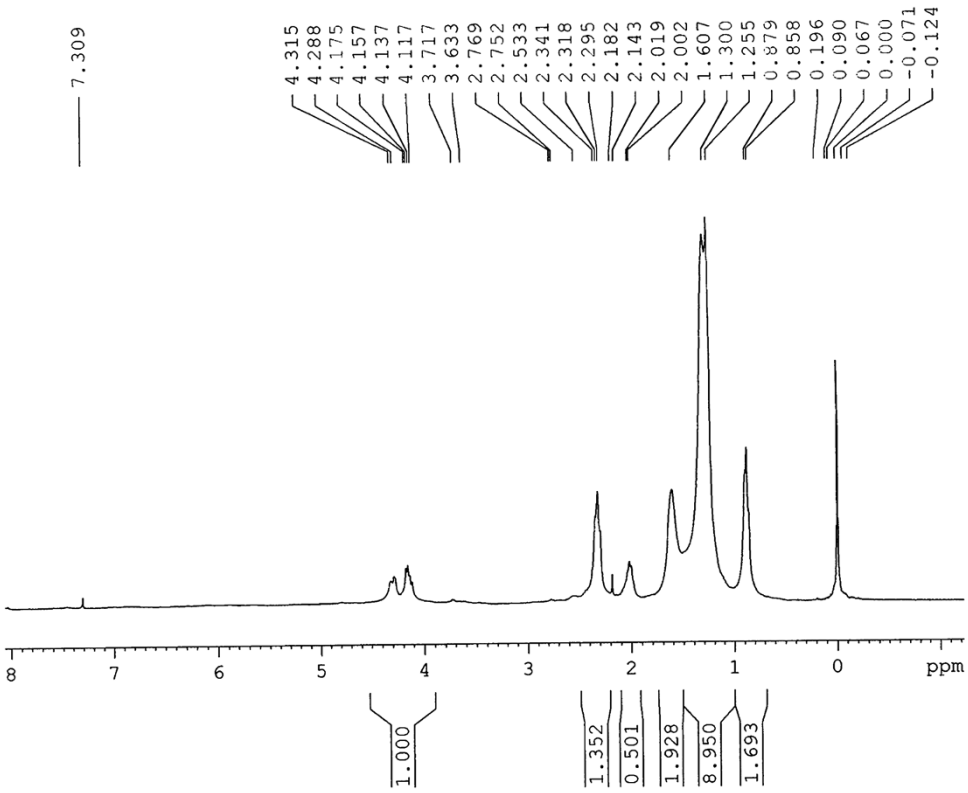

Fig. 2 ^{1}H NMR of homopolymer of SFO prepared by MI method (P-2)

better thickener compared to P-1 polymer, i.e., in comparison with P-1, base oil doped with P-2 forms better film in the lubricated surface and is more economical as far as the fuel consumption and engine lifetime are concerned.

The prepared homopolymers were tested for their effectiveness as viscosity index improvers by measuring the VI of the respective additive-doped base oils and the values are given in Table 5. The test method (ASTM D

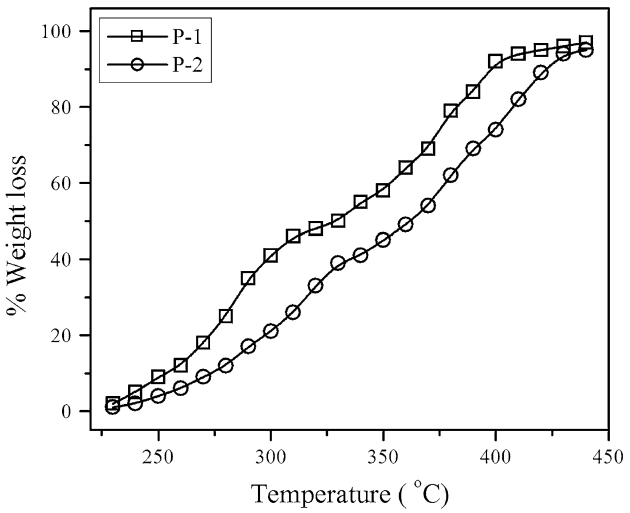

Fig. 3 TGA analysis results of the two polymers

Table 2 TGA analysis results of the polymeric additives

Temperature (°C)	Weight loss (%)	
	P-1	P-2
230	2	1
240	5	2
250	9	4
260	12	6
270	18	9
280	25	12
290	35	17
300	41	21
310	46	26
320	48	33
330	50	39
340	55	41
350	58	45
360	64	49
370	69	54
380	79	62
390	84	69
400	92	74
410	94	82
420	95	89
430	96	94
440	97	95

2270-10 method) comprises the determination of the KV of the base oils containing different doping concentrations (2–5 %, w/w) of the additives at 40 and 100 °C. As the temperature is raised, the lube oil viscosity decreases; meanwhile, the polymer molecule expands and as a result of which its hydrodynamic volume increases. The increase in the size of the solvated polymer molecules counterbalance the reduction of the viscosity of the lube oils with temperature [21]. This effect is more pronounced in case of P-2 polymer rather than P-1. The data indicate that VI increases with increasing the concentration of the prepared additives in solution [22] and the P-2 polymer-doped base oils showed higher VI values (Fig. 4) as compared to P-1 doped base oils. The results also indicated that the BO1 base oil showed better performance initially due to greater interaction with the additives. At higher concentration of the additives the BO2 base oil showed higher viscosity index.

Shear stability of both the polymers was evaluated in two base oils (Table 6). The stability of the polymers against shear decreases with increasing the PSSI values [23]. It is observed that the PVL values increase with increasing the concentration of polymer and as a result of which the PSSI values also increase. But at higher concentration of the additives the PSSI values decrease. This implies that the stability against shear decreases with increasing the polymer concentration up to a certain limit and at higher concentration it increases. The thermally prepared polymer, P-1 is more shear stable than P-2.

PPD properties of both the polymers (Table 7) as evaluated in different base stocks showed a good depression in the base stocks studied. It was found that the efficiency increases by increasing concentration of the additives and P-2 polymer showed better depression in pour point at higher concentrations than that of the P-1. Therefore, although both the polymers may be used as potential PPD for the base stocks, but the polymer prepared by microwave method is better compared to thermally made polymer.

The antiwear (AW) results showed in Table 8 indicate that with increase in the applied load WSD decreases and P-2 showed lower scar diameter compared to P-1 in both the base oils (BO1 and BO2). With the increase in concentration of the additives the scar diameter value also decreases. Since larger wear scar diameter indicates severe wear, thus the P-2 additive possessed higher wear-resistance properties than P-1 and the base oils (Fig. 5).

Analysis of biodegradability test result

Table 9 presents biodegradability test results obtained using disc diffusion method and soil burial test method. Polymers of SFO prepared by two different methods showed significant biodegradability against the fungal pathogen, *Alternaria alternata*. Result of soil burial test also indicated the similar extent of biodegradability. It was further confirmed by the shift of IR frequency of the ester carbonyl after the test is over. The commercial acrylate-

Table 3 Intrinsic viscosity, viscometric constant and molecular weight values (g mol^{-1}) determined by Mark–Houwink equation and GPC

Samples	Intrinsic viscosities		Viscometric constants			Average molecular weight values				
	$[\eta]_h$	$[\eta]_k$	k_h	k_k	$k_h + k_k$	M_h	M_k	$M_w \times 10^4$	$M_n \times 10^4$	PDI
P-1	6.784	6.667	0.367	0.126	0.493	29,797	29,090	3.1	3.02	1.026
P-2	6.973	6.762	0.335	0.13	0.465	30,949	29,661	3.21	3.1	1.035

h and *k* refers to Huggins and Kraemer Equations, respectively, *PDI* polydispersity index

Table 4 Physical properties of base oils

Properties	BO1	BO2
Density (g cm^{-3}) at 40 °C	0.840	0.941
Viscosity at 40 °C in cSt	6.708	24.229
Viscosity at 100 °C in cSt	1.774	4.016
Viscosity index	80.05	89.02
Cloud point (°C)	−5	−8
Pour point (°C)	−3	−6

based additives are non-biodegradable and do not respond to this test. The test result for biodegradability (DD and SBT) of homopolymer of dodecylacrylate (HDDA) along with the same for P-1 and P-2 is depicted in Table 9. Test results are positive with P-1 and P-2, but as was also reported earlier [15], HDDA does not show any weight loss under identical experimental conditions and thus confirmed its non-biodegradable nature.

Experimental

Materials

Refined sunflower oil (almost 87 % unsaturation) was collected from S K Oil Industries (India) and its fatty acid profile is given in Table 1. BZP (GC 98 %), obtained from Loba Chemie Pvt. Ltd. (India), was recrystallized from $CHCl_3$–MeOH before use. Base oils (BO1 and BO2) were collected from IOCL, Dhakuria, West Bengal, India. The fungal specimens were collected from Department of Microbiology, North Bengal University, West Bengal, India.

Synthesis of the polymer

The polymerization of SFO was performed by two different processes; conventional thermal procedure and greener microwave irradiation (MI) method. The details of synthetic and purification procedure of the additive are discussed below and also mentioned in Table 10.

Thermal polymerization

Synthesis of homopolymer of SFO by thermal method (P-1) was performed at 90 °C in a four necked round bottom flask for 6 h without adding any solvent. The flask was fitted with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. 10 g of the monomer was introduced in it and heated at 90 °C for 30 min. Then, 0.1 % BZP was added to it as an initiator and the mixture was heated at 90 °C with continuous stirring. The reaction occurs via radical mechanism. After the desired time, the flask was cooled to room temperature, and to terminate the polymerization the reaction mixture was poured into methanol with stirring until the precipitation was completed. It was then purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40 °C.

Microwave-assisted polymerization

Polymer of SFO by MI method (P-2) [24] was synthesized in a focused mono-mode microwave oven (CEM corporation, Matthews, NC, USA) applying 300 WT for 30 min at 90 °C by adding 0.1 % (w/w) BZP as initiator. The same amount of monomer (SFO) with 0.01 g BZP was taken in

Table 5 Viscosity index (VI) and thickening (THK) values

Sample	Base oil	Percentage (w/w) of the additives in different base oils							
		2 %		3 %		4 %		5 %	
		THK	VI	THK	VI	THK	VI	THK	VI
P-1	BO1	2.761	113	3.822	126	5.177	131	6.208	131
	BO2	1.01	101	1.567	127	2.19	163	3.135	205
P-2	BO1	2.841	121	3.935	131	5.432	128	6.807	131
	BO2	1.093	103	1.619	130	2.259	164	3.198	207

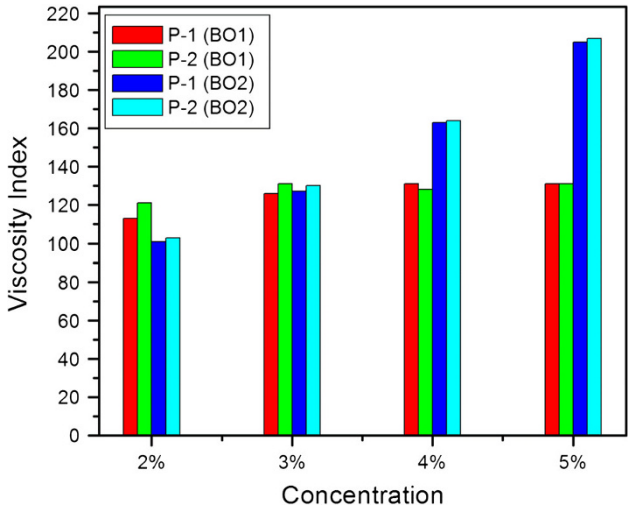

Fig. 4 VI values of the two additive-doped base oils (BO1 and BO2) at different percentage (w/w) of additive concentrations

vial and sealed with a Teflon septum. Then argon was bubbled through the solution to get oxygen-free atmosphere. The reaction mixture was magnetically stirred at 90 °C with microwave heating for 30 min applying 300 WT without any solvent, which was subsequently quenched by quickly cooling to room temperature and purified following the procedure as mentioned above. The polymerization reaction took place via radical mechanism.

Measurements

Spectroscopic measurements

The IR absorption was recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400–4,000 cm^{-1}.

Table 7 Pour points of the polymeric additives in different base oils

Additives	Base oils	Pour points (− °C) of the base oils blended with additives in different percentage (w/w)				
		0 %	2 %	3 %	4 %	5 %
P-1	BO1	−3	−6	−9	−12	−15
	BO2	−6	−9	−12	−15	−15
P-2	BO1	−3	−6	−9	−15	−18
	BO2	−6	−9	−12	−15	−18

1H NMR spectra were recorded quantitatively in Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. The sample solutions were prepared in deuterated chloroform ($CDCl_3$) and TMS was used as reference material.

Viscometric measurements

Viscometric measurements were carried out at 40 °C in toluene solution using Ubbelohde OB viscometer as per the method discussed earlier [14].

Thermogravimetric analysis (TGA)

The thermal stability was measured in terms of percent degradation of weight of the polymers with the increase in temperature (10 °C min^{-1}) by Shimadzu TGA-50 thermobalance in air using an alumina crucible.

Solubility analysis

Solubility of the prepared polymers in lube oil was investigated before testing their effectiveness as viscosity index improvers. The solubility test took place by dissolving one

Table 6 Shear stability of the polymer-doped base oils (BO1 and BO2)

Base oils	Conc. (%)	KV				PVL		PSSI	
		Before shear		After shear					
		P-1	P-2	P-1	P-2	P-1	P-2	P-1	P-2
BO1	1	2.125	2.137	2.012	2.011	5.318	5.896	32.19	34.71
	2	2.282	2.32	2.105	2.121	7.756	8.578	34.84	36.45
	3	2.401	2.428	2.172	2.185	9.538	10.01	36.52	37.16
	4	2.515	2.517	2.209	2.208	12.167	12.28	41.3	41.59
	5	2.588	2.617	2.271	2.282	12.249	12.8	38.94	39.74
BO2	1	4.371	4.404	4.214	4.201	3.592	4.609	44.23	52.32
	2	4.696	4.729	4.326	4.311	7.879	8.839	54.41	58.63
	3	5.116	5.169	4.395	4.401	14.093	14.86	65.55	66.61
	4	5.738	5.77	4.562	4.551	20.495	21.13	68.29	69.5
	5	6.612	6.656	5.002	5.015	24.350	24.65	62.02	62.16

Table 8 Antiwear properties of the SFO polymers

Polymers	Base oils	Wear scar diameter of the base oils at different levels of additive concentrations (in percentage, w/w)									
		Load: 147 ± 2 N (15 ± 0.2 Kgf)					Load: 392 ± 2 N (40 ± 0.2 Kgf)				
		0 %	1 %	2 %	3 %	4 %	0 %	1 %	2 %	3 %	4 %
P-1	BO1	0.981	0.955	0.940	0.937	0.934	0.961	0.931	0.925	0.918	0.917
	BO2	1.116	0.996	0.982	0.978	0.973	0.985	0.965	0.957	0.949	0.944
P-2	BO1	0.981	0.951	0.938	0.927	0.921	0.961	0.928	0.922	0.916	0.911
	BO2	1.116	0.982	0.976	0.968	0.964	0.985	0.961	0.953	0.945	0.942

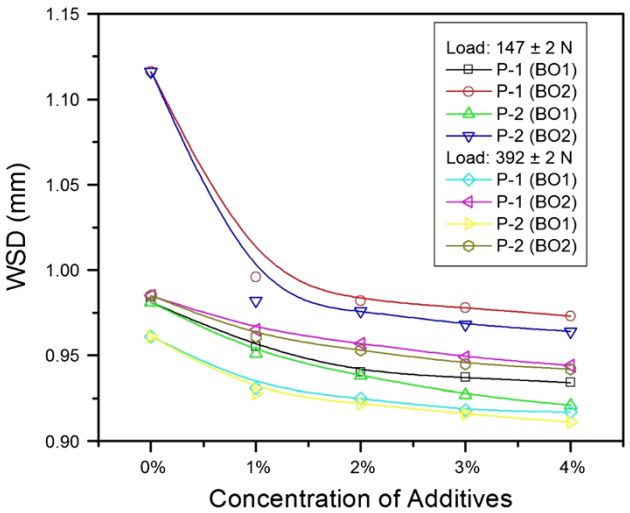

Fig. 5 Antiwear performance of the additive-doped base oils (BO1 and BO2) evaluated as wear scar diameter (mm)

Table 9 Result of biodegradability test by disc diffusion method, soil burial test for polymeric additives

Disc diffusion method					Soil burial test
Polymers	CC Wt. loss (%)	FE Wt. loss (%)	AA Wt. loss (%)	CG Wt. loss (%)	Microorganism Wt. loss (%)
P-1	0	0	36	0	20
P-2	0	0	38.7	0	26.7
HDDA	0	0	0	0	0

CC, FE, AA and CG are different pathogens used in the DD test. HDDA is homopolymer of dodecylacrylate

gram of the polymer in hundred grams of additive-free base oils. The (1 g/100 g) mixture has been allowed to stand overnight. This time was enough to produce the required swelling for the polymer. The mixture was agitated by a Teflon-covered magnetic stirrer for 20 min at 60 °C to disintegrate the gel. To test homogeneity and thermodynamic stability of the mixture, viscosity of two different samples from each solution was measured.

Evaluation of thickening property

Kinematic viscosity (KV) of the base oils and that of the polymer-doped base oils in different concentrations (2–5 %) was evaluated at 40 °C according to ASTM D445-12 method. Thickening power of the polymer was determined by evaluating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.

Evaluation of pour point

The pour point of the base oils (BO1and BO2) at different percent of doping concentrations (w/w) of the additives was evaluated using the WIL-471 cloud and pour point test apparatus model 3 (India) according to ASTM D97-11 method.

Evaluation of viscosity index

KV of the base oils containing different concentrations of the additives was determined at 40 and 100 °C. Each sample was measured three times to minimize the error. Finally, the viscosity index was determined according to ASTM D-2270-10 method.

Evaluation of permanent shear stability index (PSSI)

Shear stability of the VM is one of the important criteria that determine its suitability in a lubricant formulation. The shear stability of the doped additive has strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions, experienced by the lubricant while in use. The loss of viscosity of a lubricant under shear can be of two kinds, namely a temporary viscosity loss (TVL) or a permanent viscosity loss (PVL) [23]. PVL is similar to TVL, except that the viscosity loss is measured by KV before and after shear. The PVL values are more frequently expressed in terms of permanent shear stability index (PSSI) or simply SSI, according to ASTM D6022-01 as follows:

Table 10 Experimental details for the synthesis of SFO polymer

Monomer and its quantity	Method	Solvent	Initiator	Temperature	Reaction time	Purification	Yield (%)
SFO (10 g)	Thermal	–	BZP (0.01 g)	90 °C	6 h	Reprecipitation	78
SFO (10 g)	MI	–	BZP (0.01 g)	90 °C (300 wt)	30 min	Reprecipitation	86

$$\text{PVL}\ (\%) = (V_i - V_s)/V_i \times 100 \quad \text{PSSI} = (V_i - V_s/V_i - V_0) \times 100$$

where V_0 = KV of the base fluid before addition of polymer, V_i = KV of unsheared oil, V_s = KV of sheared oil. KV of fresh toluene and sheared polymer solution in toluene was determined by ASTM D-445 procedure, respectively.

AW properties

The AW properties were evaluated by Four-ball wear test apparatus (FBWT) according to ASTM D 4172-94 method [25] applying two different weld loads, 147 and 392 N at 75 °C for 30 min. The rotating speed of the ring was 1,200 rpm. The wear scar diameter (WSD), a parameter for the determination of antiwear performance of the oils, of the two base oils blended with the additives at different concentration levels was measured in two different applied loads.

Biodegradability test

Disc diffusion (DD) method

Biodegradation of the prepared polymer samples by DD method was tested against four different fungal pathogens namely *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA) and *Colletotrichum gloeosporioides* (CG). 1.5 g of each of the polymer sample was incubated in a Bacteriological Incubator apparatus at 37 °C for 30 days. All the glass apparatus and culture media were autoclaved before use. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. The fungal growth was confirmed by a change of yellow to blackish. After 30 days, polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed.

The soil burial test (SBT)

The SBT was conducted as per ISO 846:1997 method. 1.5 g of each of the additive samples was taken to produce a film and then buried in soil [26]. The soil was collected from North Bengal University campus having 25 % moisture and pH 7.2. The test was carried out for 90 days at 38 °C with the relative humidity 50–60 %. After the time period the sample films are recovered, washed (with chloroform), purified and finally dried. The dried samples were weighed. Percentage weight loss (PWL) of the polymeric additives was calculated and given under:

$$\text{PWL} = [(M_0 - M_1)/M_0] \times 100$$

where M_0 is the initial mass and M_1 is the remaining mass after SBT and subsequent drying till constant weight.

Conclusions

Comparison on the basis of PPD properties, AW properties and the determined VI of the additive blended base oils indicated that the performance of the SFO polymer prepared by microwave method is better than the polymer prepared by thermal method. Thermal stability of P-2 is higher as compared to P-1. However, both of them are found more or less equally effective as thickeners for the base oils studied. The shear stability of P-2 is lower than P-1. In general, it is observed that the values of viscosity index, thickening power and pour point increase with increasing concentration. The studies also indicate that VI values of the additive-doped base oils depend on the composition of the base oil. Both of the additives showed significant biodegradability by SBT and DD tests which were not expected for commercial acrylate-based additives and this is the main advantage of SFO additives. Therefore, it may be concluded that the more economical microwave irradiated synthetic method for synthesis of homopolymer of SFO is not only a greener cost-effective approach but also a better performing one.

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Conflict of interest The authors declare that they have no competing interests.

Authors' contributions PG designs the overall work. GK carried out the synthesis, experimental work. Performance evaluation of the additives was done by both PG and GK. The manuscript was written by GK. Correction and revision of the manuscript was done by PG. All the authors read and approved the final manuscript.

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